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The Tried, the True, and the New — Getting More Pulp from Chips
Modifications to the Kraft Process for Increased Yield

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THE TRIED, THE TRUE, AND THE NEW - GETTING MORE PULP FROM CHIPS -Modifications to the Kraft Process for Increased Yield

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ABSTRACT

Ever since kraft pulping started around the turn of the century, researchers and practitioners have been manipulating the process and chemistry to maximize delignification and increase pulp yield. As less wood becomes available to the paper industry, better yields are of increased importance.

Early work focused on modifications to the kraft process with multiple liquor injection and impregnation techniques to minimize the alkali degradation of cellulose and hemicellulose. Significant yield increases are possible when the carbohydrates are stabilized against alkali attack. Additives that produce yield benefits are borohydride, polysulfide, and anthraquinone. Hydrogen sulfide treatment of chips is also effective.

Some yield advantages are possible with modern-day modified batch and continuous cooking, but the primary application has been for extended delignification.

Additional improvements in yield will have to come with better control of chip quality and genetic engineering of trees to make them more readily pulped.

INTRODUCTION

Like most manufacturing industries, the paper industry is particularly sensitive to the costs of its raw materials. Efforts have been underway to maximize the yield of fiber from chemical pulping processes ever since the industry began relying on wood as its primary raw material.

In the early part of the century, as the U.S. paper industry expanded into the South with the development of southern pine pulping by the kraft process, the supply of wood for papermaking seemed unlimited. However, even in the 1920s, concerns were raised by those with foresight who called upon paper companies to assume stewardship for their raw material base in order to assure their survival.[1] As we near the end of this century, once again there is concern for the long-term supply of wood raw material for our mills.

The competition for land and forest resources is intensifying worldwide. The restriction in the supply of wood fiber in the U.S. Pacific Northwest has been well known for years, but other parts of the country such as the U.S. South are beginning to feel the pinch of more limited fiber sources. The situation in the South is primarily due to significant increases in demand accompanied by decreased growth rates. On a worldwide basis, a physical surplus of wood fiber exists in many areas but the available supply is shrinking.[2]

The future of the paper industry will be the minimum-impact mill. Minimum-impact not only means a reduction in emissions, but also a reduction in raw material consumption by maximizing the yield of manufacturing processes.[3]

There is certainly room for improvement in pulp yields when one considers that the average extractive-free composition of N. American softwoods is 43% cellulose, 28% hemicellulose, and 29% lignin, while the average composition of hardwoods is 43% cellulose, 35% hemicellulose, and 22% lignin.[4] For a lignin-free bleached pulp, the theoretical yield for softwood is 71% and 78% for hardwoods. In practice, kraft pulping results in yields of only about 60% of the theoretical.

This paper is a review of what has been tried and what has worked over the years to improve the yield of fiber by modifying the basic kraft pulping process or wood raw material.

EARLY KRAFT PROCESS MODIFICATIONS

Ever since the development of alkaline pulping by Watt and Burgess[5] and the subsequent discovery by Eaton[6] and later refinement by Dahl[7] that addition of sulfides would accelerate the process, researchers have been trying to minimize the degradation and loss of carbohydrates for better fiber strength and improved yield.

Early on it was recognized that the strong alkalinity of the kraft process was necessary for significant dissolution of lignin, but that the consequence was a corresponding loss of carbohydrates that were susceptible to alkali attack. The idea of manipulating the chemical concentration to minimize the unfavorable reactions in kraft cooking occurred to several researchers. Impregnation of chips with cooking liquor prior to actual cooking was tried and claimed to have benefits in increased yield of fiber from wood in addition to better chemical economy. Mill trials in 1922 with impregnation of jack pine with cooking liquor in a hydrostatically filled digester were reported to result in a yield gain of 4.6%.[8] At a similar time, laboratory and mill trials were done with impregnation of chips by black liquor in an effort to improve chemical efficiency by making use of the residual alkali in the liquor. Besides a reduction in chemical use and evaporator requirements, a yield increase per cord of wood of 7 to 10% was claimed.[9]

The control of the alkali concentration during the course of soda or kraft cooking was recognized as having several advantages, including a reduced degradation of cellulose. An extensive study by Bray and Curran in 1933 investigated the effect of chemical concentration on the rate of delignification and the quality of pulp in both soda and kraft cooking of several species.[10] For kraft cooking of Loblolly pine, the screened yield went from 39.8 to 34.5% as the total chemical concentration was increased from 70 to 137 g/l. In this case, the total chemical charge based on wood was high, about 30%. For kraft cooking of Douglas fir, an increase in chemical concentration from 70 to 100 g/l at a 20% total chemical charge on wood decreased the screened yield from 46.3 to 44.0%.

Additional work on the effect of chemical ratio and concentration on kraft pulping of Douglas fir by Schwartz and Bray showed that as the liquor chemical concentration increased, the yield decreased, while an increase in chemical to wood ratio from 15 to 60% also had a significant negative effect on yield.[11] In this work, the authors reached the following conclusions about the most advantageous process conditions for fiber quality. These included cooking at the lowest possible temperature, with an infinite chemical to wood ratio, and the lowest possible concentration. However, process economics would demand that cooking should proceed at the highest possible temperature, the lowest chemical ratio possible, and the highest concentration to obtain the lowest cost pulp.

A practical means to control the chemical concentration during the cook was described by Ross in 1933 and consisted of a digester system incorporating a liquor reservoir whereby alkali could be periodically injected during the cook.[12] The only example cited claimed a screened yield of 53% at a lignin content of 1.43% for injection cooking of poplar. A similar digester system was disclosed by Wells in 1934.[13] In this case, liquor was added either periodically or continuously. The process was claimed to regulate the cooking liquor concentration so that active chemical is always present but never higher than a critical concentration that would be detrimental to the fiber. This critical concentration of active chemical for kraft pulping was said to be no more than 3 lbs. as Na_2O/100 lbs. liquor or more preferably from 1-2 lbs./100 lbs. liquor. No specific examples of yield improvement were given.

Based on their studies of the effects of chemical concentration, Schwartz and Bray proposed the continuous flow of preheated liquor through the digester.[14] This served to speed the rate of reaction considerably and shorten the cooking time. With concentrations of total chemical from 30 to 52 g/l, the total yield exhibited a straight-line relationship with permanganate number. However, at a higher concentration of 90 g/l, a lower yield of about 3% at an equal permanganate number was obtained.

A later study using continuous liquor flow in batch cooking was done by Yllner *et al.*[15] They found that with alkali concentrations from 0-20 g/l NaOH at a constant 10 g/l Na_2S, there was no difference in yield at a constant lignin content, but an increase in alkali concentration to 35 g/l resulted in a yield decrease of about 4%. The analysis of dissolved carbohydrates from the spent liquor showed that carbohydrate dissolution begins almost immediately even at low alkali, and that 20% is already lost before any significant lignin removal takes place.

Westcott and Field described another system for continuous liquor flow.[16] In this process, a single liquor accumulator served to keep liquor flowing continuously through a series of batch digesters and returned to the accumulator. Provisions were also made for both black liquor and white liquor to be added so that the liquor could be refortified to keep the concentration within a range of 10-20 g/l as Na_2O. The process was claimed to result in less degradation of the pulp, though no specific yield data were given.

A continuous digestion system employing cocurrent flow of a low concentration liquor was proposed by Obenshain.[17] This liquor is recirculated at a rate from 10 to 100 times faster than the movement of chips through the digester. The liquor is refortified in the recirculation loop, but the concentration is always kept below 20 g/l. The process was claimed to produce pulp in the same time and temperature profile as a batch cook but with higher yield and viscosity. In the example cited, oak cooked to a K no. of 13.7 produced a yield of 48% in a batch process, while the continuous process with low concentration circulating liquor resulted in a yield of 53% at the same permanganate number.

In the 1950s, another impregnation process for batch digesters was introduced.[18] This was known as the Va-Purge Process and involved presteaming chips in a digester under pressure then rapidly relieving the pressure. This purge cycle was accomplished twice. Following the purge cycles, white and black liquors were introduced into the digester where penetration was quite rapid due to air being eliminated from the chips by the purging. The rapid penetration of liquor was also claimed to provide the possibility of vapor-phase cooking .[19] The Va-Purge process was claimed to increase screened pulp yield by a significant reduction in screen rejects due to better penetration of the chips by the cooking liquor. Trials on spruce wood showed that while "conventional kraft" and Va-Purge produced the same total yield at a permanganate number of 16.2, the Va-Purge process resulted in a 90% reduction in rejects from 2.5 to 0.28%.[20]

Studies by Christiansen and Legg investigated injection cooking along with the Va-Purge process.[21] In tests with Jack pine, Douglas fir, and southern pine, they found that when using injection of white liquor at a sulfidity of 33% that there was no significant improvement in pulp quality for bleachable-grade pulps and slight improvement for higher yield pulps. They explain the difference in results with those of earlier investigators regarding the benefits of injection cooking to be a function of the higher sulfidity used in these experiments compared with earlier studies. It was proposed that at a sulfidity of 33%, sufficient protection of the cellulose is obtained without any added benefit from liquor injection.

KRAFT PULPING ADDITIVES

As the chemistry of the kraft process was better understood and the mechanisms for degradation and loss of polysaccharides in alkaline solutions were realized, the search was on for ways to stabilize the cellulose and hemicelluloses against alkaline attack, resulting in higher pulp yields. One way to stabilize the polysaccharides against alkali degradation is to convert the carbonyl groups with a reducing or an oxidizing agent, preventing further peeling reaction.

Sodium dithionite, $Na_2S_2O_4$, has been known as an effective reductive bleaching agent for groundwood and mechanical pulp. A study by Jayme and Wörner in 1952 reported that up to a 4-5% yield increase on spruce was obtained with a high concentration of dithionite.[22] A subsequent investigation, however, by Regnfors showed little effect.[23]

Hartler studied the effect of another reducing agent, sodium borohydride, $NaBH_4$, on stabilizing polysaccharides in kraft pulping of pine.[24] When 0.5% $NaBH_4$ on wood was added to the cooking liquor, the rate of delignification was increased, and the total pulp yield at the same Roe no. was improved from 47 to 50%. An analysis of the pulps showed that the glucomannan content of the pulp was 80% of that originally in the wood, while the corresponding kraft cook only retained 30% of the glucomannan. The content of xylan was somewhat lower in the borohydride cook, which was attributed to the higher glucomannan content interfering with the reabsorption of xylan onto the fiber surface in the later stages of the cook. Further studies of the mechanisms of borohyride stabilization of carbohydrates in pine showed that pretreatment of chips with an alkaline solution of borohydride at 1% $NaBH_4$ on wood was also effective in increasing pulp yields.[25] Kraft pulping of spruce with borohydride also resulted in a substantial yield increase from increased retention of glucomannan with little change in cellulose yield, and a slight decrease in xylan yield.[26]

In the kraft pulping of birch, the dissolution of lignin was considerably increased with the addition of 2% $NaBH_4$ at an equivalent active alkali.[27] When the alkali concentration for the borohydride cooks was adjusted to achieve the same degree of delignification as the kraft cooks, the total yield was increased from 52.6 to 59.2% with a corresponding 17% decrease in active alkali.

Despite the impressive yield gains with borohydride added to kraft cooks, the chemical cost has made its use prohibitive.

Other researchers investigating sulfur chemistry began to realize the ability of elemental sulfur or polysulfides to stabilize polysaccharides. Hägglund found that sulfur addition to a soda liquor increased the yield about 5%.[28] Berthiér in 1953 described the pulping of maritime pine with kraft liquors containing polysulfides.[29]

In 1960, a patent was issued to Kibrick *et al.* for cooking of wood with alkali polysulfides.[30,31] Yield increases of 1 to 15% were claimed when using liquors with polysulfides. Somewhat better results were claimed when the source of the polysulfide was sulfurated potash ($K_2S{\cdot}K_2S_2O_3$) instead of sodium polysulfide. In the examples cited, southern pine chips were cooked to a permanganate number of 18 and total yield of 46% with conventional kraft liquor. With alkali polysulfide added, the yield was 52% at a permanganate number of 24, or with sulfurated potash added, a yield of 49% at a permanganate number of 18 was obtained.

Peckham and May pulped a mix of southern pine chips with conventional kraft liquor as well as a soda-sulfur liquor.[32] At an active alkali charge of 17%, the kraft pulp resulted in a yield of 48.6% at a permanganate no. of 24.6 while the soda-sulfur pulp at the same active alkali and a polysulfide level of 1.1% on o.d. wood had a yield of 50.4%. A comparison of the strength results showed the soda-sulfur pulp to be somewhat lower in strength, particularly tear.

A more systematic study on pulping of spruce by Kleppe and Kringstad showed that yield increases of 1 to 8% were possible with polysulfide additions of 1 to 7% on wood.[33] The yield increase was found to be primarily due to better retention of the glucomannan with just a slight increase in cellulose retention and a decrease in the xylan content, paralleling the results found with borohydride pulping. The authors also noted that the polysulfide will start to disproportionate at temperatures above 130°C. The polysulfide pulps were easier to beat with higher tensile strength but lower tear strengths.

The mechanism of yield improvement by polysulfide was investigated by Alfredsson *et al.*[34] They confirmed that the aldehyde end groups formed during cleavage of the carbohydrate chains are oxidized to aldonic acid end groups, resulting in a stabilization against further peeling.

Sanyer and Laundrie studied the variables of polysulfide pulping with respect to the yield, strength, and chemical mechanisms.[35] At an addition rate of 12% polysulfide on wood, the yield was increased from 50 to 61% at 50 Kappa no. and from 44.5 to 53.5% at 35 Kappa no. Spruce and balsam fir showed similar yield increases of 11-22% on pulp with 3-12% polysulfide. Yield increases with Douglas fir were slightly less. The majority of the yield increase was again found to be a higher retention of glucomannan with some increases also in cellulose and xylan retention. The strength properties were similar except for a lower tear. The use of low digestion temperatures, pre-impregnation, slow rate of heatup, and short or thin chips increased the efficiency of the polysulfide.

Venemark discussed the practical implications of producing polysulfide in a mill.[36] The simple addition of sulfur to the liquor as is done in the lab is not possible in the mill without a way to get rid of the excess sulfur in the spent liquor. Several methods of converting sulfide in green liquor to polysulfide were discussed, and all involved significant increased costs. The need to develop an inexpensive way to produce polysulfide in kraft liquors was expressed.

The decomposition of polysulfide at temperatures higher than 130°C and in alkali solutions led Clayton and Sakai to propose a multistage process whereby chips are first impregnated with a pure polysulfide solution under mild temperature conditions.[37] Further work led to the development of a three-stage process using an ammonium polysulfide solution and ammonium hydroxide in the impregnation stage, followed by a second stage to promote carbohydrate stabilization where ammonium hydroxide is added and the chips heated to 175°C for 30-45 minutes.[38] The chips are then followed by a kraft pulping stage. For a Kappa no. 35 pulp, the yield increase from the ammonium-based treatment with 1.3% polysulfide was 2.3% over conventional kraft. A corresponding single-stage treatment with 1.5% polysulfide resulted in a yield increase of 1.5%. The maximum yield increase achieved was 8% over the kraft cook with 3.5% polysulfide added in the ammonia system.

When the development of a catalyzed oxidation reaction to convert sulfide to polysulfide was realized, it became practical to use polysulfide in kraft pulping and more commercial applications were initiated.[39]

Pretreatment of chips with hydrogen sulfide prior to kraft pulping was investigated as a possible alternative to polysulfide. Vinje and Worster pretreated hemlock, Douglas fir, and aspen with 0.6 to 1.4% hydrogen sulfide on wood for 40 minutes at 127°C.[40] The addition of an alkaline buffer such as sodium carbonate or green liquor was found to have an advantageous effect on the yield. A standard kraft or soda cook followed the pretreatment. Yield improvements of 6% on wood were realized at equal permanganate numbers. The yield increase was primarily the result of increased glucomannan for the softwood and an increase in xylan and cellulose for aspen. The hydrogen sulfide pretreatment was also believed to allow for more efficient penetration of the chips by the kraft liquor, resulting in fewer rejects and about 2.5% less alkali for the same amount of delignification.[41]

The search for additives to improve alkaline pulping led Bach and Fiehn to the discovery of a compound, anthraquinone-2-mono-sulfonate (AMS), which was effective in small amounts in increasing the reaction rate and improving pulp yields for soda pulping.[42] Subsequent research on 300 similar types of compounds resulted in the discovery by Holton that unmodified anthraquinone (AQ) was very effective in increasing the delignification rate while preserving the yield in both soda and kraft cooks.[43,44,45] Under equal pulping conditions, 1% (on wood) AQ added to a soda cook of spruce, pine, and fir decreased the Kappa no. from 105 to 27.5 with a 4% drop in yield where normally an 11% decrease would be expected. Soda-AQ pulping was promoted as a replacement for kraft because it now had a comparable reaction rate and pulp yield.

In Japan, another quinone additive has been used, 1,4-dihydro-9,10-dihydroxy anthracene or DDA. It was claimed to give better results than AQ, and unlike AQ, it is soluble in liquor solutions. Mill trials with 0.044% DDA added to kraft cooks resulted in a yield increase of about 0.8% at the same Kappa no. along with a reduction in pulping time of 10 minutes.[46] The yield increase plus the shorter time resulted in a mill production increase of 9%.

Many studies, trials, and mill experiences using AQ in alkaline cooks have followed with the benefits in yield and accelerated delignification well-documented.[47]

Shortly after the introduction of AQ as another pulping additive, it was tried in combination with polysulfide (PS). Kleppe reported on mill trials in the production of sack kraft grades.[48] The addition of 0.05% AQ to a PS cook resulted in an additional 1.1% yield increase on wood above the 3.5% yield increase over conventional kraft at 60 Kappa no. that is obtained with PS alone. The addition of 0.05% AQ to a kraft cook resulted in a yield increase of 0.8% over conventional kraft.

Additional studies by Green and Smith showed that the yield gains from the addition of both AQ and PS in kraft pulping were additive, and in some cases, synergistic where the total yield increase was greater than the sum of the yield increases from PS and AQ separately.[49] For a spruce/pine mixture, the respective yield increases for 0.10% AQ or 1.35% PS were 2.1 and 2.2%, while the yield increase from both was 4.3%. For Douglas fir, no yield increase was measured for 0.02% tetrahydroanthraquinone (THAQ) alone, while a 1.7% increase was obtained with 1.5% PS. The corresponding PS-THAQ cook resulted in a 2.5% yield increase. A mixed Japanese hardwood furnish with 0.02% THAQ improved the yield 0.2%, while 1.28% PS improved the yield 1.1%, and the combination PS-THAQ resulted in a yield gain of 1.3%.

A number of studies since have confirmed the synergistic effect of PS and AQ on increasing kraft pulp yields.

Surfactants have been tried as an additive to kraft cooking liquor to increase the liquor penetration into chips and improve the uniformity of pulping. An increase in yield may be expected as a result of a decrease in screen rejects. Chen reported that the use of a surfactant in an unbleached mill allowed the Kappa no. to be increased 10 points at the same reject level.[50] A screened yield increase from 50 to 52.3% was expected as a result.

MODIFIED COOKING

In the 1970s, Swedish researchers began to combine the present knowledge of kraft pulping chemistry and kinetics to develop kraft process modifications that would maximize delignification while preserving pulp strength and yield. The process came to be called extended delignification or modified cooking and was based on several pulping chemistry principles.[51,52] These concepts were the alkali concentration should be as low and as even as possible throughout the cook; the sulfide concentration should be as high as possible in the initial part of the cook and during the transition from the initial to the bulk phase of delignification; and the dissolved lignin concentration should be kept as low as possible during the latter part of the cook.[53] These principles were applied in the operation of continuous digesters where multiple liquor additions and countercurrent liquor flow were possible to allow for a more even alkali profile and removal of dissolved organics in the late stages of the cook. However, the requirement for initial high sulfide concentration was not as easily accomplished.

The analysis of pulp samples from laboratory cooks simulating mill-scale operation of cooking with a modified alkali profile was done by Teder and Sandstrom to determine the pulp yields.[54] They found that over the Kappa no. range from 35-20, the modified cook resulted in an increase of carbohydrate yield of 0.5%. Further testing showed that a yield gain of about 1% was achieved with the modified alkali profile at an equivalent Kappa no.[55]

Sjöblom investigated the effect of modified continuous cooking on pulp yields with regards to xylan reabsrption.[56] In conventional cooking it is known that dissolved xylan will reabsorb onto pulp fibers in the later stages of the cook thus increasing total yield. The countercurrent liquor flow in the later stage of a modified continuous cook will remove dissolved xylan and other organics and limit reabsorption. The study showed that continuous liquor flow cooks where the dissolved material is being removed had about 1.7% lower yield than standard batch kraft cooks. However, a simulation of counter-current liquor flow where dissolved xylan was introduced into an earlier stage of the cook showed that some reabsorption apparently took place since there was no yield loss compared to the standard cook.

The original modified cooking process was changed by applying another principle for improved pulp quality, pulping with lower temperatures. Additional white liquor added to the bottom circulation of a continuous digester allows for longer cooking times. With the longer times, the maximum cooking temperature can be lowered. This is the basis of extended modified or isothermal cooking. Because of more uniform cooking, this process is claimed to result in a yield increase of 0.5 to 1.0% for SW and somewhat higher for HW.[57]

Despite modest yield gains at equal Kappa nos., the real application of modified cooking has been for extended delignification. When cooking to lower Kappa nos., yield is lost even though the loss may be less than what would occur with conventional cooking to low Kappa nos.

To counteract the yield loss, several studies and trials were done with the addition of polysulfide and anthraquinone to modified cooks. Jiang reported on the addition of PS to the white liquor for extended modified cooking of southern pine.[58] The yield improvement was 3% with 2% PS at a Kappa no. of 30 and a 2% yield improvement was realized in the range of 12-20 Kappa no.

Lloyd *et al.* reported that that laboratory simulation of modified cooking of radiata pine with 2% PS added to a high sulfidity impregnation liquor increased yield by 2% at a 20 Kappa no. over conventional kraft and modified cooks.[59] Interestingly, there did not appear to be any yield advantage for modified cooking with and without high sulfide liquor impregnation. There was also no yield advantage for these modified cooks over conventional kraft.

Griffin *et al.* studied the effect of AQ and PS in modified cooking of southern pine.[60] When AQ was added to the impregnation stage, the yield was increased by 1 to 1.5% at the same Kappa no. When the AQ addition was split between the impregnation and cocurrent stages, a 0.5 to 1.0% yield increase was seen. No yield increase was achieved when all the AQ was added to the cocurrent zone. With PS added to the impregnation stage at a charge of 0.97%, a 1% yield increase was achieved. When both AQ (0.1%) and PS (0.97%) were added to the impregnation stage, the yield increase was 2 to 2.5%.

A more recent comparison of the addition of PS to both modified and isothermal cooks was reported by Hakanen and Teder.[61] In this case, they simulated the generation of PS in a mill by starting with a higher than normal sulfidity liquor so that even after conversion of HS^- ions to polysulfide or S_n, there is still sufficient HS^- concentration to improve the selectivity of the cook. For modified cooking, the addition of 1.6% PS increased the carbohydrate yield 1.2% at a Kappa no. of 24, while 1.7% PS in the isothermal cook increased the yield 1.5% at a Kappa no. of 19. For a conventional continuous cook, 1.6% PS resulted in an increase of 3% in carbohydrate yield at a Kappa no. of 46. The lower yield increases for the modified cooks may be due to a higher hydroxide ion concentration later in the cook. Additionally, the countercurrent liquor flow has the effect of removing dissolved polysaccharides that would otherwise tend to reprecipitate on the fibers.

At the same time developments were taking place in modifying the continuous process, batch processes were being re-examined to make them competitive with the continuous process. Initially, batch modifications were done to increase the energy efficiency. This was accomplished by using the residual heat from spent liquor to preheat the chips and the white liquor for subsequent cooks. The use of black liquor for impregnation was found to have some beneficial effects. The high sulfidity of the liquor helps to retard carbohydrate degradation and permit extended delignification.[62] Andrews claimed a 1% yield increase for extended batch displacement cooking by virtue of better cooking uniformity and fewer screen rejects.[63]

Tikka and Kovasin studied the benefits of displacement batch cooking with a series of hanging baskets in mill digesters.[64] They compared displacement batch cooking with black liquor impregnation and cold blow discharge with conventional batch cooks but also with cold blow discharge. At equal Kappa nos., the yield increase for the displacement cooking was about 1.5%. It was believed this was the result of reduced cooking time, high liquor-to-wood ratios with low alkali concentration, and more uniform cooking.

In a study of the effect of alkali charge on batch displacement cooks of southern pine, Abuhasan *et al.* found that the displacement cooks were able to obtain the same Kappa no. as conventional batch cooks at a lower alkali level.[65] The conventional and displacement cooks resulted in similar yields at an equal Kappa no. except for when the active alkali was 18% or higher in which case the displacement cooks had 0.5 to 1% lower yield. When the active alkali was reduced from 18 to 15% for displacement cooks, there was an increase of 1.5% in yield. In another study, the addition of AQ to the hot black liquor phase of batch displacement cooks increased the yield by about 1% over a Kappa no. range of 14-23.[66]

RAW MATERIAL MODIFICATIONS

An area for improvement in most mills that can pay benefits in increased yield is chip quality. The critical dimension of chip thickness in the uniform penetration of cooking chemical has been known for some time. Non-uniform cooking leads to increased screen rejects and lower screened yields. Tyler and Edwards demonstrated that the tendency to produce rejects increases in proportion to chip thickness squared.[67] The effect of chip thickness screening for both conventional and displacement batch cooking was studied by Tikka *et al.* in a series of hanging basket experiments.[68] With displacement cooking, thickness screened chips produced a total yield increase of 1% at Kappa 30 and 2% at Kappa 15 over conventionally screened chips. For the conventional kraft process, the yield increase was about 0.5% over the range of Kappa 35-15. The screen rejects were reduced by half with thickness screening for both cooking methods. The combination of displacement cooking and thickness screening was claimed to reduce total rejects by 75%. Gullichsen and co-workers in a study of chip pulping uniformity showed that thinner chips need less chemicals, produce less rejects, and result in better yield selectivity.[69,70] Chips greater than 2 mm thick begin to show uneven delignification, while chips greater than 5 mm are poorly delignified in the center. Impregnation of chips with white liquor followed by cooking with a low alkali liquor improved uniformity, resulting in an increased screened yield. An increase in bleached pulp yield of 2 to 3% is possible when pulping chips with a thickness of 4 mm or less along with thorough impregnation with liquor.

As long as the industry continues to use the strongly alkaline kraft process, there are limits to the fiber yields that can be achieved. The maximum yield increase over standard kraft cooking seems to be approximately 10% with stabilization of the polysaccharides against alkali reactions. The next generation of yield improvements will have to come from modifications to the raw material itself. Getting more fiber yield from harvested timberlands is a goal of forest biologists. The genetic manipulation of trees for enhanced properties such as faster growth and herbicide resistance is already being practiced.[71] Modification of tree properties for easier delignification is a promising area of research. The discovery of abnormal lignin in a mutant loblolly pine may lead to better knowledge of lignin biosynthesis and ways to manipulate it.[72] Programs are underway to change the lignin composition in eucalyptus[73] and radiata pine.[74]

Kraft pulping of poplar with genetically altered lignin was done with 20% active alkali and 25% sulfidity.[75] A 2-year-old control sample produced a pulp with an 18.7 Kappa no. and 45.9% yield. For one transgenic sample, the yield was 48.8% at a kappa no. of 14.5, and for another sample, the yield was 47.4% at a Kappa no. of 15.6. Further developments in tree engineering could lead to pulping processes with milder conditions and less carbohydrate degradation.

CONCLUSIONS

Alkaline pulping methods such as the kraft process will always result in some degradation and loss of non-cellulosic carbohydrates. Significant yield gains result from the stabilization of carbohydrates against alkali attack. Changing the liquor concentrations by injection, impregnation, or continuous flow to minimize alkali attack have limited benefits in yield improvement.

Polysulfide and anthraquinone are the most economically and chemically viable additives for improving pulp yield in the kraft process by stabilizing carbohydrates. They function in an additive or synergistic fashion. Maximum yield increases appear to be on the order of 4 to 6%.

Surfactants may have some benefit by promoting better liquor penetration and decreasing rejects.

Modified cooking, either batch or continuous, results in no or modest gains in yield at a given Kappa no. The preservation of pulp viscosity and strength down to lower Kappa nos. makes them systems of choice when lower Kappa nos. are needed.

Better control of chipping and chip screening to produce uniform, thin chips can increase yield by a reduction in rejects.

Breaking the yield barrier in kraft pulping will require significant changes to the composition of the wood raw material through genetic engineering.

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